

# (12) UK Patent Application (19) GB (11) 2 091 166 A

- (21) Application No 8201002  
 (22) Date of filing 14 Jan 1982  
 (30) Priority data  
 (31) 225642  
 (32) 16 Jan 1981  
 (33) United States of America (US)  
 (43) Application published  
 28 Jul 1982  
 (51) INT CL<sup>3</sup>  
 B32B 5/02  
 C25B 13/02 //  
 B32B 27/02 27/04 27/08 27/10  
 C25B 1/46  
 (52) Domestic classification  
 B5N 0502 2702 2704 2708 2710  
 C7B 145 551 552 553 554 CA  
 (56) Documents cited  
 GB 2043108 A  
 (58) Field of search  
 B5N  
 C7B  
 (71) Applicants  
 E.I. du Pont de Nemours and Company,  
 Wilmington,  
 Delaware 19898,  
 United States of America.  
 (72) Inventors  
 Raimund Heinrich Silva  
 (74) Agents  
 J.A. Kemp & Co.,  
 14 South Square,  
 Gray's Inn,  
 London, WC1R 5EU,  
 England.

(54) Membrane, electrochemical cell, and electrolysis process

(57) An ion exchange membrane which comprises at least a layer of fluorinated polymer which contains -COONa or -COOK groups, and optionally a layer of fluorinated polymer which contains -SO<sub>3</sub>Na or -SO<sub>3</sub>K groups, which membrane contains therein a microporous polytetrafluoroethylene sheet which has been stretched in at least one direction, and which membrane has been fabricated by melt lamination, is described. The membrane may optionally have an external reinforcing fabric adhered to one surface thereof. Such membrane can be used as the separator between the compartments of a chloralkali cell, and such a cell operates at low voltage, high current efficiency, and low power consumption.

GB 2 091 166 A

## SPECIFICATION

## Membrane, electrochemical cell, and electrolysis process

5 *Background of the invention* 5

Fluorinated ion exchange polymers having carboxylic acid and/or sulfonic acid functional groups or salts thereof are known in the art. One principal use of such polymers is as a component of a membrane used to separate the anode and cathode compartments of a chloralkali electrolysis cell. Such membrane can be in the form of a reinforced or unreinforced film or laminar structure.

10 It is desirable for use in a chloralkali cell that a membrane provides for operation at low voltage and high current efficiency, and thereby at low power consumption, so as to provide products of high purity at low cost, especially in view of today's steadily increasing cost of energy. It is also desirable that the membrane be tough, so as to resist damage during fabrication and installation in such a cell. As films of the best available ion exchange polymers have low tear strength, it has been found necessary to strengthen them by 15 fabricating membranes with reinforcement therein, such as a reinforcing fabric.

However, use of reinforcement within the membrane is not totally beneficial. A deleterious effect is that use of reinforcement such as fabric results in a thicker membrane, which in turn leads to operation at higher voltage because the greater thickness has a higher electrical resistance. Efforts to lower the resistance by using thinner films in fabricating reinforced membranes are often unsuccessful because the film ruptures in 20 some of the windows of the fabric during membrane fabrication, resulting in a membrane with leaks. (By "windows" is meant the open areas of a fabric between adjacent threads of the fabric.) A membrane which leaks is undesirable as it permits anolyte and catholyte to flow into the opposite cell compartment, thereby lowering the current efficiency and contaminating the products made. Additionally, thick layers of polymer at the junctions of threads in a reinforcing fabric also constitute regions of high resistance. (By "junctions" is 25 meant the crossover points where threads in the warp meet threads in the weft.)

It is a principal object of this invention to provide an ion exchange membrane which operates at low voltage and high current efficiency, and thereby at low power consumption, and yet has good tear resistance. Another object is to provide a thin, tough ion exchange membrane. Other objects will be apparent hereinbelow.

30 *Summary of the invention* 30

Briefly, according to the invention, there is provided a melt fabricated ion exchange membrane which contains at least a layer of fluorinated polymer which contains  $-\text{COONa}$  or  $-\text{COOK}$  functional groups, and which membrane contains therein a sheet of microporous polytetrafluoroethylene which has been stretched 35 in at least one direction.

More specifically, in one aspect of the invention there is provided an ion-exchange membrane which comprises a layer of fluorinated polymer which has  $-\text{COOM}$  functional groups, where M is Na or K, and, completely embedded therein, a microporous polytetrafluoroethylene sheet which has been stretched in at least one direction, said membrane having been fabricated by melt lamination.

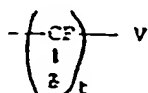
40 In another aspect of the invention there is provided an ion-exchange membrane which comprises a first layer of a first fluorinated polymer which has  $-\text{COOM}$  functional groups, a second layer of a second fluorinated polymer which has  $-\text{SO}_3\text{M}$  functional groups, where M is Na or K, and, completely embedded therein, a microporous polytetrafluoroethylene sheet which has been stretched in at least one direction, said membrane having been fabricated by melt lamination.

45 There are also provided according to the invention an electrochemical cell having such ion exchange membrane as a component part thereof, and an electrolysis process in which such ion exchange membrane is used.

*Detailed description of the invention*

50 The membranes of the present invention are typically prepared from one or more layers of fluorinated polymer which have  $-\text{COOR}$  and/or  $-\text{SO}_2\text{W}$  function groups, where R is lower alkyl and W is F or Cl, and a web of support material.

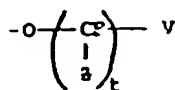
The first layer of polymer with which the present invention is concerned is typically a carboxylic polymer having a fluorinated hydrocarbon backbone chain to which are attached the functional groups or pendant 55 side chains which in turn carry the functional groups. The pendant side chains can contain, for example



60

60

groups where Z is F or  $\text{CF}_3$ , t is 1 to 12, and V is  $-\text{COOR}$  or  $-\text{CN}$ , where R is lower alkyl. Ordinarily, the functional group in the side chains of the polymer will be present in terminal

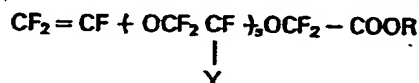


groups. Examples of fluorinated polymers of this kind are disclosed in British Patent No. 1,145,445, U.S. 4,116,888 and U.S. 3,506,635. More specifically, the polymers can be prepared from monomers which are fluorinated or fluorine-substituted vinyl compounds. The polymers are usually made from at least two monomers. At least one monomer is a fluorinated vinyl compound such as vinyl fluoride, hexafluoropropylene, vinylidene fluoride, trifluoroethylene, chlorotrifluoroethylene, perfluoro (alkyl, vinyl ether), tetrafluoroethylene and mixtures thereof. In the case of copolymers which will be used in electrolysis of brine, the precursor vinyl monomer desirably will not contain hydrogen. Additionally, at least one monomer is a fluorinated monomer which contains a group which can be hydrolyzed to a carboxylic acid group, e.g., a carboalkoxy or nitrile group, in a side chain as set forth above.

By "fluorinated polymer" is meant a polymer in which, after loss of the R group by hydrolysis to ion exchange form, the number of F atoms is at least 90% of the number of F atoms and H atoms.

The monomers, with the exception of the R group in the  $-\text{COOR}$ , will preferably not contain hydrogen, especially if the polymer will be used in the electrolysis of brine, and for greatest stability in harsh environments, most preferably will be free of both hydrogen and chlorine, i.e., will be perfluorinated; the R group need not be fluorinated as it is lost during hydrolysis when the functional groups are converted to ion exchange groups.

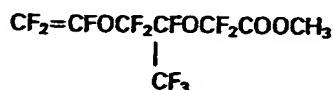
One exemplary suitable type of carboxyl-containing monomer is represented by the formula



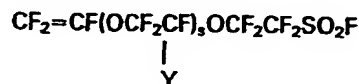
wherein

R is lower alkyl,  
Y is F or  $\text{CF}_3$ , and  
s is 0, 1 or 2.

Those monomers wherein s is 1 are preferred because their preparation and isolation in good yield is more easily accomplished than when s is 0 or 2. The compound

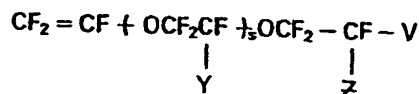


is an especially useful monomer. Such monomers can be prepared, for example, from compounds having the formula



wherein s and Y are as defined above, by (1) saturating the terminal vinyl group with chlorine to protect it in subsequent steps by converting it to a  $\text{CF}_2\text{Cl}-\text{CFCl}-$  group; (2) oxidation with nitrogen dioxide to convert the  $-\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$  group to an  $-\text{OCF}_2\text{COF}$  group; (3) esterification with an alcohol such as methanol to form an  $-\text{OCF}_2\text{COOCH}_3$  group; and (4) dechlorination with zinc dust to regenerate the terminal  $\text{CF}_2=\text{CF}-$  group. It is also possible to replace steps (2) and (3) of this sequence by the steps (a) reduction of the  $-\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$  group to a sulfinic acid,  $-\text{OCF}_2\text{CF}_2\text{SO}_2\text{H}$ , or alkali metal or alkaline earth metal salt thereof by treatment with a sulfite salt or hydrazine; (b) oxidation of the sulfinic acid or salt thereof with oxygen or chromic acid, whereby  $-\text{OCF}_2\text{COOH}$  groups or metal salts thereof are formed; and (c) esterification to  $-\text{OCF}_2\text{COOCH}_3$  by known methods; this sequence is more fully described in South African Patent No. 78/2224. Preparation of copolymers thereof is described in South African Patent No. 78/2221.

Another exemplary suitable type of carboxyl-containing monomer is represented by the formula



wherein

V is -COOR or -CN,

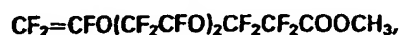
R is lower alkyl,

Y is F or CF<sub>3</sub>,

Z is F or CF<sub>3</sub>, and

s is 0, 1 or 2.

The most preferred monomers are those wherein V is -COOR wherein R is lower alkyl, generally C<sub>1</sub> to C<sub>6</sub>, because of ease in polymerization and conversion to ionic form. Those monomers wherein s is 1 are also preferred because their preparation and isolation in good yield is more easily accomplished than when s is 0 or 2. Preparation of those monomers wherein V is -COOR where R is lower alkyl, and copolymers thereof, is described in U.S. Patent No. 4,131,740. The compounds

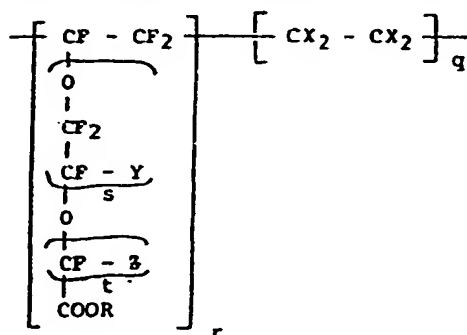


whose preparation is described therein, are especially useful monomers. Preparation of monomers wherein V is -CN is described in U.S. Patent No. 3,852,326.

Yet another suitable type of carboxyl-containing monomer is that having a terminal -O(CF<sub>2</sub>)<sub>v</sub>COOCH<sub>3</sub> group where v is from 2 to 12, such as CF<sub>2</sub>=CF-O(CF<sub>2</sub>)<sub>3</sub>COOCH<sub>3</sub> and CF<sub>2</sub>=CFOCF<sub>2</sub>CF(CF<sub>3</sub>)O(CF<sub>2</sub>)<sub>3</sub>COOCH<sub>3</sub>.

Preparation of such monomers and copolymers thereof is described in Japanese Patent Publications 38486/77 and 28586/77, and in British Patent No. 1,145,445.

Another class of carboxy-containing polymers is represented by polymers having the repeating units



wherein

q is 3 to 15,

r is 1 to 10,

s is 0, 1 or 2,

t is 1 to 12,

the X's taken together are four fluorines or three fluorines and one chlorine,

Y is F or CF<sub>3</sub>,

Z is F or CF<sub>3</sub>, and

R is lower alkyl.

A preferred group of copolymers are those of tetrafluoroethylene and a compound having the formula



where

n is 0, 1 or 2,

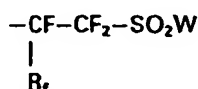
m is 1, 2, 3 or 4,

Y is F or CF<sub>3</sub>, and

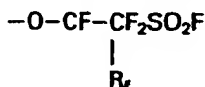
R is CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub> or C<sub>3</sub>H<sub>7</sub>.

Such copolymers with which the present invention is concerned can be prepared by techniques known in the art, e.g., U.S. Patent No. 3,528,954, U.S. Patent No. 4,131,740, and South African Patent No. 78/2225.

When a layer of sulfonyl polymer is present, it is typically a polymer having a fluorinated hydrocarbon backbone chain to which are attached the functional groups or pendant side chains which in turn carry the functional groups. The pendant side chains can contain, for example,



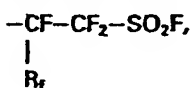
5 groups wherein  $\text{R}_f$  is F, Cl, or a  $\text{C}_1$  to  $\text{C}_{10}$  perfluoroalkyl radical, and W is F or Cl, preferably F. Ordinarily, the functional group in the side chains of the polymer will be present in terminal



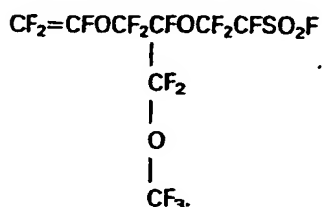
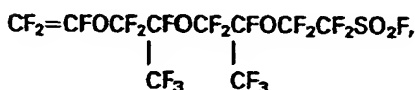
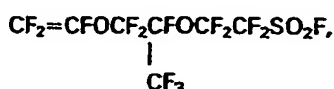
10 groups. Examples of fluorinated polymers of this kind are disclosed in U.S. Patent No. 3,282,875, U.S. Patent No. 3,560,568 and U.S. Patent No. 3,718,627. More specifically, the polymers can be prepared from monomers which are fluorinated or fluorine substituted vinyl compounds. The polymers are made from at least two monomers, with at least one of the monomers coming from each of the two groups described below.

15 At least one monomer is a fluorinated vinyl compound such as vinyl fluoride, hexafluoropropylene, vinylidene fluoride, trifluoroethylene, chlorotrifluoroethylene, perfluoro (alkyl, vinyl ether), tetrafluoroethylene and mixtures thereof. In the case of copolymers which will be used in electrolysis of brine, the precursor vinyl monomer desirably will not contain hydrogen.

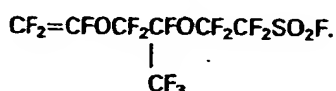
20 The second group is the sulfonyl-containing monomers containing the precursor group



25 wherein  $\text{R}_f$  is as defined above. Additional examples can be represented by the general formula  $\text{CF}_2=\text{CF—T}_k\text{—CF}_2\text{SO}_2\text{F}$  wherein T is a bifunctional fluorinated radical comprising 1 to 8 carbon atoms, and k is 0 or 1. Substituent atoms in T include fluorine, chlorine, or hydrogen, although generally hydrogen will be excluded in use of the copolymer for ion exchange in a chloralkali cell. The most preferred polymers are free of both hydrogen and chlorine attached to carbon, i.e., they are perfluorinated, for greatest stability in harsh environments. The T radical of the formula above can be either branched or unbranched, i.e., straight-chain, and can have one or more ether linkages. It is preferred that the vinyl radical in this group of sulfonyl fluoride containing comonomers be joined to the T group through an ether linkage, i.e., that the comonomer be of the formula  $\text{CF}_2=\text{CF—O—T—CF}_2\text{—SO}_2\text{F}$ . Illustrative of such sulfonyl fluoride containing comonomers are

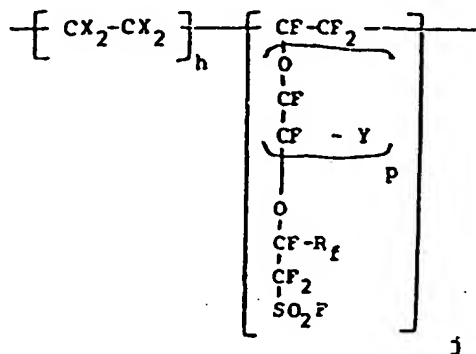


The most preferred sulfonyl fluoride containing comonomer is perfluoro(3,6-dioxo-4-methyl-7-octenesulfonyl fluoride),



60 The sulfonyl-containing monomers are disclosed in such references as U.S. Patent No. 3,282,875, U.S. Patent No. 3,041,317, U.S. Patent No. 3,718,627 and U.S. Patent No. 3,560,568.

A preferred class of such polymers is represented by polymers having the repeating units



wherein

h is 3 to 15,

j is 1 to 10,

p is 0, 1 or 2,

the X's taken together are four fluorines or three fluorines and one chlorine,

Y is F or CF<sub>3</sub>, and

R<sub>f</sub> is F, Cl or a C<sub>1</sub> to C<sub>10</sub> perfluoralkyl radical.

A most preferred copolymer is a copolymer of tetrafluoroethylene and perfluoro(3,6-dioxa-4-methyl-7-octenesulfonyl fluoride) which comprises 20 to 65 percent, preferably, 25 to 50 percent by weight of the latter.

Such copolymers used in the present invention can be prepared by general polymerization techniques developed for homo- and copolymerizations of fluorinated ethylenes, particularly those employed for tetrafluoroethylene which are described in the literature. Nonaqueous techniques for preparing the copolymers include that of U.S. Patent No. 3,041,317, that is, by the polymerization of a mixture of the major monomer therein, such as tetrafluoroethylene, and a fluorinated ethylene containing a sulfonyl fluoride group in the presence of a free radical initiator, preferably a perfluorocarbon peroxide or azo compound, at a temperature in the range 0-200°C and at pressures in the range of 10<sup>5</sup> to 2×10<sup>7</sup> pascals (1-200 Atm.) or higher. The nonaqueous polymerization may, if desired, be carried out in the presence of fluorinated solvent. Suitable fluorinated solvents are inert, liquid, perfluorinated hydrocarbons, such as perfluoromethylcyclohexane, perfluorodimethylcyclobutane, perfluorooctane, perfluorobenzene and the like, and inert, liquid chlorofluorocarbons such as 1,1,2-trichloro-1,2,2-trifluoroethane, and the like.

Aqueous techniques for preparing the copolymer include contacting the monomers with an aqueous medium containing a free-radical initiator to obtain a slurry of polymer particles in non-water-wet or granular form, as disclosed in U.S. Patent No. 2,393,967, or contacting the monomers with an aqueous medium containing both a free-radical initiator and a telogenically inactive dispersing agent, to obtain an aqueous colloidal dispersion of polymer particles, and coagulating the dispersion, as disclosed, for example, in U.S. Patent No. 2,559,752 and U.S. Patent No. 2,593,583.

A copolymer which contains different types of functional groups can also be used as a component film in making the membrane of the invention. For example, a terpolymer prepared from a monomer chosen from the group of nonfunctional monomers described above, a monomer from the group of carboxylic monomers described above, and additionally a monomer from the group of sulfonyl monomers described above, can be prepared and used as one of the film components in making the membrane.

It is further possible to use as a component film of the membrane a film which is a blend of two or more polymers. For example, a blend of polymer having sulfonyl groups in melt-fabricable form with a polymer having carboxyl groups in melt-fabricable form can be prepared and used as one of the component films of the membrane of this invention.

It is additionally possible to use a laminar film as one of the component films in making the membrane. For example, a film having a layer of a copolymer having sulfonyl groups in melt-fabricable form and a layer of a copolymer having carboxyl groups in melt-fabricable form, can also be used as one of the component films in making the membrane of the invention.

An essential component of the membrane of the invention is a layer of a first fluorinated polymer which has -COONa or -COOK functional groups, which has an equivalent weight in the range of 400 to 2000, most preferably 1000 to 1100, and which has a thickness in the range of 13 to 250 microns (0.5 to 10 mils), preferably 25 to 75 microns (1 to 3 mils).

The membrane of the invention may or may not have, in adherent contact with said layer of first fluorinated polymer, an optional component which is a layer of a second fluorinated polymer which has -SO<sub>3</sub>Na or -SO<sub>3</sub>K functional groups, which has an equivalent weight in the range of 800 to 2000, most preferably 1100 to 1200, and which has a thickness in the range of 13 to 150 microns (0.5 to 6 mils), preferably 13 to 75 microns (0.5 to 3 mils). When this second layer is present, the thickness of the first layer of first

fluorinated polymer should be 13 to 150 microns, preferably 13 to 75 microns, and the thickness of the first and second layers taken together should be in the range of 26 to 250 microns (1 to 10 mils), preferably 26 to 150 microns (1 to 6 mils).

Concerning both the polymer with carboxyl functionality and the polymer with sulfonyl functionality, above an equivalent weight of 2000, the electrical resistivity becomes too high, and below the indicated lower equivalent weight limits, the mechanical properties are poor because of excessive swelling of the polymer. The relative amounts of the comonomers which make up the polymer can be adjusted or chosen such that the polymer has a desired equivalent weight. The equivalent weight above which the resistance of a film or membrane becomes too high for practical use in an electrolytic cell varies somewhat with the thickness of the film or membrane. For thinner films and membranes, equivalent weights up to about 2000 can be tolerated. For most purposes, however, and for films of ordinary thickness, a value no greater than about 1400 is preferred.

A second essential component of the membrane is a microporous polytetrafluoroethylene sheet. This sheet can be a film or extrudate made, or treated by any means to make it, microporous. This sheet should have a thickness in the range of 2.5 to 250 microns (0.1 to 10 mils), preferably 13 to 75 microns (0.5 to 3 mils), and has open-cell porosity, with a pore size in the range of 0.01 to 20 microns, preferably 3 to 15 microns. By "pore size" is meant an average size of the pores present.

This microporous sheet is one which has been stretched in at least one direction so that it will be tough, and thus impart toughness to the membrane of the invention. Stretching results in orientation of the polymer in the sheet. The ability of the microporous sheet to provide toughness in the thin membranes of the invention is an important aspect of the invention. Use of an oriented sheet also provides a more dimensionally stable membrane. The sheet can be one which has been stretched in two mutually perpendicular directions; such sheet has both greater orientation and toughness, and provides a membrane which resists tearing in all directions.

A typical such microporous sheet is one of polytetrafluoroethylene having a microstructure characterized by nodes interconnected by fibrils, made by high-rate stretching at an elevated temperature of an unsintered, dried paste extrudate of polytetrafluoroethylene, as described in U.S. 3,962,153, and commercially available from W. L. Gore & Associates, Inc., under the trademark Gore-Tex.

If the membrane has only the first layer of first fluorinated polymer, the microporous sheet will be disposed in said first layer, and should be completely embedded therein. As employed herein, the term "completely embedded" means that the pores of the microporous sheet are filled with said first and/or second fluorinated polymer which will subsequently be converted to ion exchange polymer, but that fibrils of polytetrafluoroethylene which are part of the microporous sheet may protrude from the surface of the membrane.

If the membrane has both a first layer of first fluorinated polymer and a second layer of second fluorinated polymer, the microporous sheet can be disposed in either layer, or at the boundary of the layers, thus extending into both layers. For a membrane intended for use in a chloralkali electrolysis process, the microporous sheet will preferably be predominantly in the second layer, and most preferably entirely in the second layer, and the membrane will be employed with the second layer facing the anode of the cell. In any case, the microporous sheet is completely embedded in the resulting composite structure.

The membranes of the invention may also include a further optional component, which is woven or knitted reinforcement fabric, disposed externally on the membrane, adherent to one of the surfaces preferably to the exposed surface of the second layer described above.

In the case of woven fabric, weaves such as ordinary basketweave and leno weave are suitable. The threads of the fabric can be either monofilament or multistranded.

The threads are perhalocarbon polymer threads. As employed herein, the term "perhalocarbon polymer" is employed to refer to a polymer which has a carbon chain which may or may not contain ether oxygen linkages therein and which is totally substituted by fluorine or by fluorine and chlorine atoms. Preferably the perhalocarbon polymer is a perfluorocarbon polymer, as it has greater chemical inertness. Typical such polymers include homopolymers made from tetrafluoroethylene and copolymers of tetrafluoroethylene with hexafluoropropylene and/or perfluoro (alkyl vinyl ethers) with alkyl being 1 to 10 carbon atoms such as perfluoro (propyl vinyl ether). An example of a most preferred thread material is polytetrafluoroethylene. Threads made from chlorotrifluoroethylene polymers are also useful.

So as to have adequate strength in the fabric before lamination, and in the membrane after lamination, the threads should be of 50 to 600 denier, preferably 200 to 400 denier (denier is g/9000 m of thread).

The fabric will typically have a thread count in the range of 1.6 to 16 threads/cm (4 to 40 threads (inch)) in each of the warp and weft, preferably 3 to 10 threads/cm.

The membrane can be made from the component layers of film and the microporous sheet with the aid of heat and pressure. Temperatures of about 200°C to 300°C are ordinarily required to fuse the polymer films employed and enable the microporous sheet to become completely embedded in the film, and, when two films are used, to make the films fuse together; the temperature required may be even above or below this range, however, and will depend on the specific polymer or polymers used. The choice of a suitable temperature in any specific case will be clear, inasmuch as too low a temperature will fail to bring about embedment of the microporous sheet as evidenced by a high opacity, and will fail to effect an adequate degree of adherence of the films to each other where there are two films, and two high a temperature will

cause leaks to form. Pressures of as little as about  $2 \times 10^4$  pascals, to pressures exceeding  $10^7$  pascals can be used. A hydraulic press is a suitable apparatus for making the membrane, in which case typical pressures are in the range of  $2 \times 10^5$  to  $10^7$  pascals.

Another apparatus, suitable for continuous preparation of membrane, comprises a hollow roll with an internal heater and an internal vacuum source. The hollow roll contains a series of circumferential slots on its surface which allow the internal vacuum source to draw component materials in the direction of the hollow roll. The vacuum draws the component materials of the membrane onto the hollow roll, such that typical air pressures against the component materials in the range of  $5 \times 10^4$  to  $10^5$  pascals. A curved stationary plate with a radiant heater faces the top surface of the hollow roll with a spacing of about 6 mm (1/4 inch) between their two surfaces.

During a lamination run, porous release paper is used in contacting the hollow roll as a support material to prevent adherence of any component material to the roll surface and to allow vacuum to pull component materials in the direction of the hollow roll. Feed and takeoff means are provided for the component materials and product. In the feed means one idler roll of smaller diameter than the hollow roll is provided for release paper and component materials. The feed and takeoff means are positioned to allow component materials to pass around the hollow roll over a length of about 5/6 of its circumference. A further idler roll is provided for the release paper allowing its separation from the other materials. Takeoff means are provided for the release paper and the product membrane.

For use in ion exchange applications and in cells, for example a chloralkali cell for electrolysis of brine, the membrane should have all of the functional groups converted to ionizable functional groups. These groups are  $-\text{COOM}$  groups, and, when present,  $-\text{CO}_3\text{M}$  groups, where M is Na or K. Such conversion is ordinarily and conveniently accomplished by hydrolysis with acid or base, such that the various functional groups described above in relation to the melt-fabricable polymers are converted respectively to the free acids or the alkali metal salts thereof. Such hydrolysis can be carried out with an aqueous solution of a mineral acid or an alkali metal hydroxide. Base hydrolysis is preferred as it is faster and more complete. Use of hot solutions, such as near the boiling point of the solution, is preferred for rapid hydrolysis. The time required for hydrolysis increases with the thickness of the structure. It is also of advantage to include a water-miscible organic compound such as dimethylsulfoxide in the hydrolysis bath. The free carboxylic and sulfonic acids are convertible to salts with NaOH or KOH.

The membrane of the invention is impermeable to hydraulic flow of liquid. (A diaphragm, which is porous, permits hydraulic flow of liquid therethrough with no change in composition, while an ion exchange membrane permits selective permeation by ions and permeation of liquid by diffusion, such that the material which penetrates the membrane differs in composition from the liquid in contact with the membrane.) It is an easy matter to determine whether there is or is not hydraulic flow of liquid by a leak test with gas or liquid.

A principal use of the ion exchange membrane of the invention is in electrochemical cells. Such a cell comprises an anode, a compartment for the anode, a cathode, a compartment for the cathode, and a membrane which is situated to separate the two said compartments. One example is a chloralkali cell.

The copolymers used in the layers described herein should be of high enough molecular weight to produce films which are at least moderately strong in both the melt-fabricable precursor form and in the hydrolyzed ion exchange form.

To further illustrate the innovative aspects of the present invention, the following examples are provided.

## EXAMPLES

### Example 1

In a hydraulic press having 20 cm  $\times$  20 cm (8  $\times$  8 inch) heatable platens were placed a piece of film of a copolymer of tetrafluoroethylene and methyl perfluoro (4,7-dioxo-5-methyl-8-nonenolate) having an equivalent weight of 1050, said piece of film having a thickness of 36 to 43 microns (1.4-1.7 mils) and being circular 12.5 cm (5 inches) in diameter, and a piece of "Gore-Tex" sheet as described hereinabove, said piece of sheet having a thickness of 25 microns (1 mil), being circular 12.5 cm in diameter, and having a pore size of 0.5 micron. The assembly of film and microporous sheet was heated at 220°C under  $3.23 \times 10^6$  pascals (30,000 lb force) for 1 minute, after preheating for 1 minute. The resulting composite structure had a thickness of about 64 microns (2.5 mils), and was almost transparent, which indicated complete embedment of the microporous sheet in the layer of copolymer film. The composite structure was placed in a mixture of 74 wt. % water, 15 wt. % dimethylsulfoxide and 11 wt. % potassium hydroxide at 80°C for 1 hour to hydrolyze the  $-\text{COOCH}_3$  groups, thus providing an ion exchange membrane having  $-\text{COOK}$  groups. The membrane was thoroughly washed with water and mounted in a small chloralkali cell. The cell was operated for 8 days at 80°C, 31 amps/dm<sup>2</sup>, and 20 wt. % exit brine concentration to produce caustic at 32 wt. % at a current efficiency of 93.7-96.3%, voltage of 3.59-3.73 volts, and a power consumption of 2523-2568 kwh/metric ton.

During the electrolysis, the functional groups of the membrane became  $-\text{COONa}$  groups.

By way of comparison a copolymer film like that described above, except that it was 51 microns (2 mils) thick, and having no microporous sheet therein, was hydrolyzed as above, soaked in 30 wt. % aqueous NaOH for 2 hours, mounted in a small chloralkali cell and operated for 8 days under the same conditions as above to produce caustic at a current efficiency of 94.9-99.9%, voltage of 4.02-4.18 volts, and a power consumption of 2790-2863 kwh/metric ton.



*Example 2*

In the hydraulic press described in Example 1 were placed a piece of film of a copolymer like that of Example 1, 12.5 cm in diameter, 25 microns thick, a piece of fabric, 12.5 cm in diameter, and between the film and the fabric, a piece of "Gore-Tex" sheet as described hereinabove, 12.5 cm in diameter, 25 microns thick, pore size of 3 to 5 microns. ((The fabric had 10 threads/cm (25 thread/inch) of 200 denier polytetrafluoroethylene yarn in the warp, and 10 threads/cm (25 threads/inch) of 400 denier polytetrafluoroethylene yarn in the weft, in a leno weave, and was 175 microns (7 mils) thick)). The assembly of microporous sheet, fabric and film was heated at 270°C under  $1.06 \times 10^5$  pascals (10,000 lb force) for 1 minute, after preheating for 1 minute. The resulting composite structure had excellent mechanical strength, and was free of leaks when tested under a vacuum of  $1.65 \times 10^4$  pascals (25 inches of mercury). The composite structure was placed in an aqueous solution containing 32 wt. % NaOH and 10 wt. % methanol at room temperature for 2 hours to hydrolyze the  $-\text{COOCH}_3$  groups, thus providing an ion exchange membrane having  $-\text{COONa}$  groups. The membrane is useful as a separation between the compartments of electrochemical cells.

*Industrial applicability*

The ion exchange membrane of the present invention is technically advanced over membranes of the prior art. It exhibits improved performance characteristics when used as membrane in a chloroalkali cell, including operation at low voltage and high current efficiency, and thus at lower power consumption. There is accordingly a substantial saving in operating costs resulting from the lowered consumption of power. The membrane of the invention also provides for less gas blinding by chlorine on the anolyte side of the membrane during brine electrolysis.

The ion exchange membrane of the invention can also be used in the electrolysis of water to hydrogen and oxygen, and in Donnan dialysis and electrodialysis processes.

## CLAIMS

1. An ion-exchange membrane which comprises a layer of fluorinated polymer which has  $-\text{COOM}$  functional groups, where M is Na or K, and, completely embedded therein, a microporous polytetrafluoroethylene sheet which has been stretched in at least one direction, said membrane having been fabricated by melt lamination.
2. A membrane according to claim 1 wherein said layer is 13 to 250 microns thick, and said fluorinated polymer is perfluorinated polymer which has an equivalent weight of 400 to 2000.
3. A membrane according to claim 1 or 2, wherein said sheet is 2.5 to 250 microns thick and has a pore size of 0.01 to 20 microns.
4. A membrane according to claim 1 wherein said layer is 13 to 75 microns thick, said perfluorinated polymer has an equivalent weight of 1000 to 1100, and said sheet is 13 to 75 microns thick and has a pore size of 3 to 15 microns.
5. A membrane according to any one of the preceding claims wherein said sheet has been stretched in two mutually perpendicular directions.
6. A membrane according to any one of the preceding claims wherein said perfluorinated polymer is a copolymer of tetrafluoroethylene and



7. A membrane according to any of claims 1 to 5 wherein said perfluorinated polymer is a copolymer of tetrafluoroethylene and  $\text{CF}_2 = \text{CFO}(\text{CF}_2)_3\text{COOM}$ ,



8. A membrane according to any one of the preceding claims wherein said membrane further comprises an external support fabric adhered thereto, said fabric being woven or knitted, and consisting of filaments of perfluorocarbon polymer.

9. An ion-exchange membrane which comprises a first layer of a first fluorinated polymer which has  $-\text{COOM}$  functional groups, a second layer of a second fluorinated polymer which has  $-\text{SO}_3\text{M}$  functional groups, where M is Na or K, and, completely embedded therein, a microporous polytetrafluoroethylene sheet which has been stretched in at least one direction, said membrane having been fabricated by melt lamination.

10. A membrane according to claim 9 wherein each of said first and second layers is 13 to 150 microns thick and said two layers have a total thickness of 26 to 250 microns, said first and second fluorinated polymers are each perfluorinated polymers, said first perfluorinated polymer has an equivalent weight of 400 to 2000, and said second fluorinated polymer has an equivalent weight of 800 to 2000.

11. A membrane according to claim 9 or 10 wherein said sheet is 2.5 to 250 microns thick and has a pore size of 0.01 to 20 microns.

12. A membrane according to claim 10 wherein each of said first and second layers is 13 to 75 microns thick and said two layers have a total thickness of 26 to 150 microns, said first perfluorinated polymer has an equivalent weight of 1000 to 1100, said second perfluorinated polymer has an equivalent weight of 1100 to 1200, and said sheet is 13 to 75 microns thick and has a pore size of 3 to 15 microns.

13. A membrane according to claim 9, 10, 11 or 12 wherein said sheet has been stretched in two mutually perpendicular directions.

14. A membrane according to any one of claims 9 to 13 wherein said sheet lies at least predominantly in said second layer.

15. A membrane according to any one of claims 9 to 14 wherein said second fluorinated polymer is a copolymer of tetrafluoroethylene and



16. A membrane according to any one of claims 9 to 15 wherein said first fluorinated polymer is a copolymer of tetrafluoroethylene and



17. A membrane according to any one of claims 9 to 15 wherein said first fluorinated polymer is a copolymer of tetrafluoroethylene and  $\text{CF}_2 = \text{CFO}(\text{CF}_2)_3\text{COOM}$ ,  $\text{CF}_2 = \text{CFOCF}_2\text{CFOCF}_2\text{COOM}$  or  $\text{CF}_2 = \text{CFOCF}_2\text{CFO}(\text{CF}_2)_3\text{COOM}$ .



18. A membrane according to any one of claims 9 to 17 wherein said membrane further comprises an external support fabric adhered thereto, said fabric being woven or knitted, and consisting of filaments of perfluorocarbon polymer.

19. A membrane according to claim 18 wherein said support fabric is adhered to said second layer.

20. A membrane according to claim 1 or 9 substantially as described with reference to Example 1 or 2.

21. An electrochemical cell which comprises an anode compartment, a cathode situated within said cathode compartment, and, between said compartments, a membrane as claimed in any one of the preceding claims.

22. A process which comprises the electrolysis of brine in a chloroalkali cell which comprises an anode, an anode compartment, a cathode, a cathode compartment, and a fluorine-containing cation exchange membrane which separates said compartments, to form caustic and chlorine wherein there is used as said membrane a membrane as claimed in any one of claims 1 to 20.